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LUBRICITY OF JET FUELS

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LUBRICITY PROPERTIES
OF
HIGH-TEMPERATURE
JET FUELS

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FOREWORD

This report was prepared by the Advanced Lubrication Project, Products Research Division, Esso Research and Engineering Co. at Linden, N.J. under Contract AF33 (615) 2828. This program is administered by the Air Force Aero Propulsion Laboratory, Research and Technology Division, Air Force Systems Command with Arthur F. Levenstein, 1/LT, ISAF as coordinator.

This report covers work conducted from 15 November, 1966 to 15 February, 1967.

ABSTRACT

Corrosive wear, i.e., wear in which the primary cause is oxidation of the metal surface, is shown to be an important factor in jet fuel lubricity. A literature survey has been made, which indicates considerable confusion and disagreement.

Additional hydrocarbons have been evaluated. Most of them give more wear and friction when oxygen and water are present. Indene and 1-methyl naphthalene are exceptions, giving high wear in dry, inert atmospheres. No explanation has been found for these differences.

High-temperature tests in the presence of oxygen often given lower wear than tests at lower temperatures. This has been shown to be due to the formation of oxidation products that have good lubricity.

I. INTRODUCTION

Recent work under this Contract has showed that friction and wear are greatly influenced by the presence of dissolved oxygen and water, and that fuels differ not only in their inherent lubricity but also in their response to oxygen and water. Thus, in a steel-on-steel system, paraffinic hydrocarbons and the commercial fuels give more wear and friction when oxygen and water are present. This is corrosive wear and its severity increases at high oxygen concentrations, high humidity, high temperature and high loads. Blanketing with an inert gas greatly reduces not only wear but also the effect of temperature and load.

Certain heavy aromatic hydrocarbons, typified by methyl-naphthalene, have quite different behavior. At low concentrations (1-2%) in paraffinic fuels, they are good lubricity additives, reducing both wear and friction markedly. However, by themselves, they are not much better than the paraffinics when compared in air, and give very high wear when run in an inert gas. This behavior is not found with lighter aromatics such as benzene or substituted benzenes.

The picture is a confusing one of synergistic effects, marked interaction between variables, wear and friction going in opposite directions, and many anomalies.

This present report deals mostly with this hydrocarbon-atmosphere interaction. Because the literature is contradictory on the effect of oxygen on wear, it has been reviewed once again, in considerably greater depth than in the last Annual Report. This forms the next section of this report. Friction and wear data on many hydrocarbons and hydrocarbon mixtures in various atmospheres are then presented. The effect of anti-icing additive has also been investigated, and some fuels with field experience have been evaluated.

II. LITERATURE SURVEY

A. Basic Processes

Dissolved water and oxygen are critically important to wear and friction of jet fuels. It is worthwhile to consider their solubility properties and other aspects that could be pertinent here.

We have already shown that the action of both oxygen and water is at the rubbing surface. Oxidation of the hydrocarbons, or similar chemical changes in the liquid, are not the phenomenon involved. Therefore, the pertinent question is how much oxygen or water is actually available at the rubbing surface.

For permanent gases such as oxygen, the availability will depend on several factors: the solubility of oxygen in the hydrocarbon (the Bunsen coefficient), the partial pressure of oxygen in the surrounding atmosphere, the diffusion rate of oxygen through the hydrocarbon, and the rate of oxygen depletion by reaction with the surface or (particularly at higher temperatures) with the hydrocarbon. Thus, oxygen availability is a dynamic equilibrium between a driving force (partial pressure times the Bunsen coefficient) and a depletion factor (reaction with metal or hydrocarbon). If the depletion factor is large, the diffusion rate can then be important. Each of these factors will be considered in turn.

Oxygen Solubility

The solubility of oxygen in various hydrocarbons differs considerably. Oxygen is most soluble in paraffins and least soluble in aromatics, the difference being 3-4:1. This difference among hydrocarbons is a function of the solubility parameter, which is the square root of the cohesive energy density:

$$\delta = \left(\frac{\Delta H - RT}{V} \right)^{1/2}$$

where δ = solubility parameter
 ΔH = heat of vaporization of the solvent
 V = molar volume of the solvent
 R = gas constant
 T = absolute temperature

The relationship between solubility parameter and gas solubility is given in Figure 1, taken from Reference 1. However, for precise purposes it is best to measure the gas solubility directly, using for example, gas chromatography. (For a review of older methods, see Reference 2.) In all the n-paraffins, the solubility of oxygen is essentially the same, even more so than the solubility parameter would indicate. Isoparaffins have greater solubility for oxygen than do n-paraffins, olefins and aromatics have less. This is in accordance with Hildebrand's solubility theory: oxygen has a very low solubility parameter and thus resembles isoparaffins most and aromatics least.

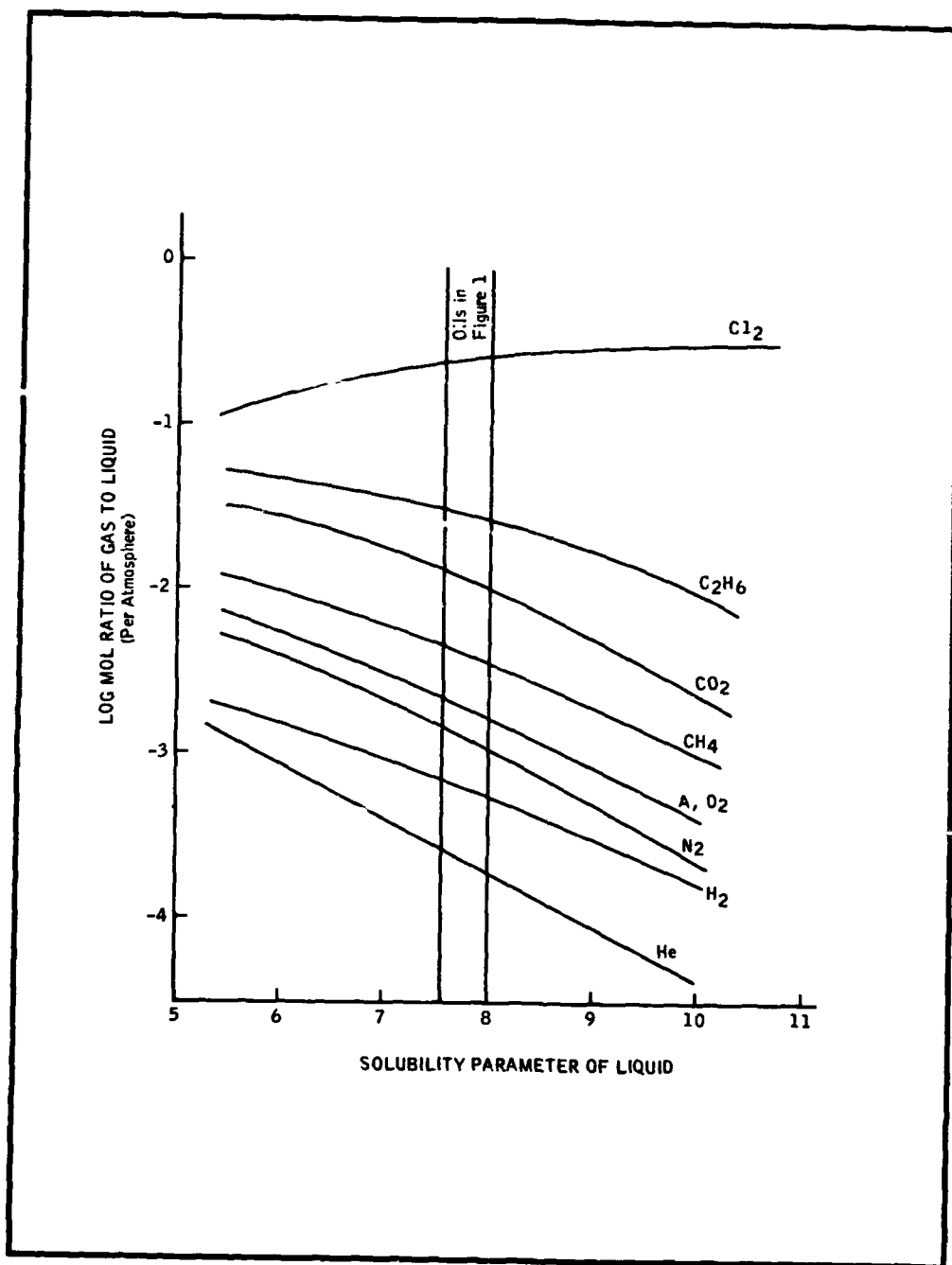


FIGURE 1
SOLUBILITY OF GASES IN VARIOUS LIQUIDS AT 25°C

The solubility of any single gas is usually expressed as the Ostwald coefficient or the Bunsen coefficient, which are based on Henry's Law. Henry's Law states that the solubility of a gas is directly proportional to the partial pressure of that gas in the atmosphere above the liquid:

$$C = kP.$$

For atmospheric pressures and below, this law is quantitatively exact. If P is 760 mm and C is expressed as volume of gas at STP per volume of liquid, then C is Bunsen's coefficient. Ostwald's coefficient is similar except that the volume of gas is at the actual temperature. Ostwald's coefficient is therefore independent of partial pressure. For our purposes, the Bunsen coefficient is more meaningful, for we are interested in the number of molecules available at the rubbing surface and not the volume they would occupy in the gas phase.

The solubility of most gases change with temperature. For petroleum oils this has been reduced to a single chart (3), reproduced as Figure 2. This is a plot of the Ostwald coefficient vs. temperature. (Had the Bunsen coefficient been plotted, the lines would have a somewhat greater negative slope.)

Very soluble gases, such as CO₂, show decreasing solubility, whereas less soluble gases, such as helium, show increasing solubility with temperature. Argon and oxygen have very similar solubility characteristics and neither show much change with temperature. This is a happy coincidence, for we can observe the effect of temperature on wear directly, without having to make corrections for the amount of oxygen dissolved.

Water Solubility

Unlike oxygen, water has a large solubility parameter and therefore is most soluble in aromatics and least soluble in paraffins and isoparaffins. In all cases, the water molecules are widely separated from each other and do not exhibit hydrogen bonding. Hence, water behaves more like a gas of molecular weight 18 than like a liquid. However, at temperatures below 100C, water can also be emulsified and it is very difficult to distinguish between a microemulsion and a true solution. Small amounts of polar materials can greatly increase the amount of dissolved or emulsified water. Therefore, measurements of water solubility in highly-purified liquids may not have much pertinence in practical fuels.

Total water content is best measured by the Karl Fischer method, but care must be taken to insure that the water content does not change between the time of the lubricity test and the time of analysis. Diffusion of water in hydrocarbons is quite rapid.

It is obvious that the relative humidity of the surrounding atmosphere is the factor controlling dissolved water content. Normally humidity is not controlled during wear tests and so it remains a major cause of irreproducibility. In our work it is controlled either at 0% or 100% RH. The gas from compressed gas cylinders, having been made by liquefaction, is extremely dry -- so much so that passing it through a conventional desiccant will actually increase its moisture content. Saturated gas is conveniently obtained by bubbling through water.

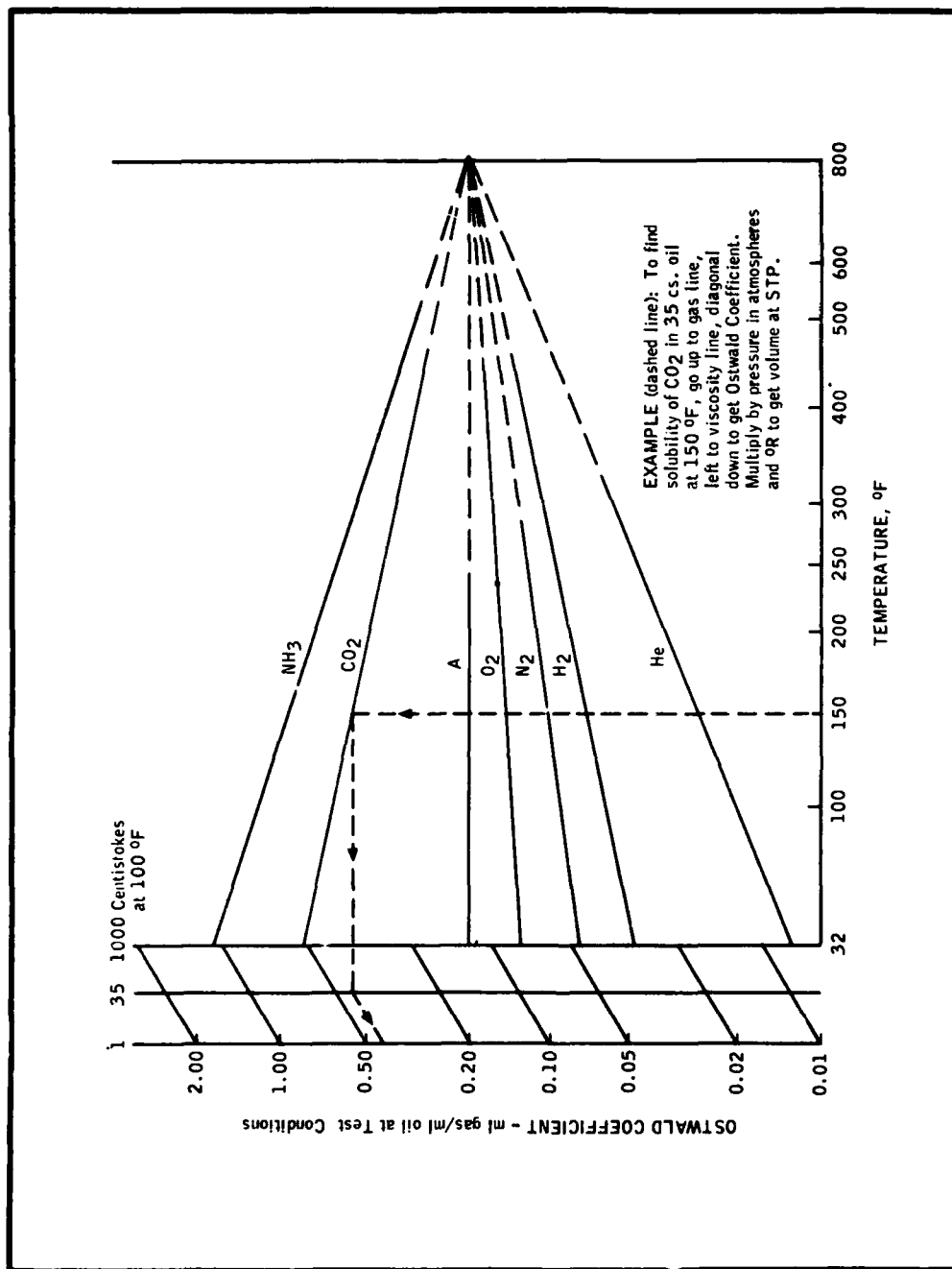


FIGURE 2
SOLUBILITY OF GASES IN PETROLEUM OILS

Reaction of Oxygen with Metal Surfaces

The kind of wear encountered here is believed to be corrosive wear. That is, the primary cause of wear is the reaction of the metal surface to form iron oxide. The oxide wears away, exposing fresh metal surface which can then oxidize further. This kind of wear is an entirely different mechanism from abrasive wear or scuffing wear. It is akin to fretting corrosion except that the reactions are in reverse order. In fretting corrosion, the first process is a "molecular plucking" or adhesive wear, in which a metal particle is removed from the surface by vibration; it quickly oxidizes to form wear debris. In corrosive wear, the first process is the oxidation to form a loosely-bound oxide which is then worn away.

Corrosive wear is a common form of wear in engine cylinders. The cylinder walls are cooled by the water jacket on one side, and exposed to combustion products on the other. These combustion products, consisting in part of water and corrosive acids, can condense on the walls and cause corrosion. It has been shown (4) that when the wall temperature drops below the dew point of the combustion products, wear increases suddenly and severely.

Corrosive wear is therefore dependent on the amount of oxygen and water vapor available, the ability of the oil additives to protect the surface, the temperature of the surface, and the degree of corrosion resistance of the metal.

As will be shown later, there is some disagreement as to the exact mechanism of corrosive wear. An alternate explanation is that the oxide particles formed by corrosion are themselves abrasive. Being harder than the steel surface, they give excessive abrasive wear. In either explanation, however, the primary cause is the initial attack of the iron by oxygen.

Diffusion

Preliminary calculations have shown that diffusion could easily be the controlling factor in corrosive wear. The amount of corrosive wear would deplete the oxygen supply at the metal surface, and the rate of diffusion would not be enough to replenish the supply.

However, the actual situation is quite complicated, involving a changing area of corrosion, a very thin layer of liquid, and an oxygen concentration that changes with both direction of travel and film thickness. Hence, a complete mathematical analysis is being made to determine if the reaction is diffusion-limited, and what effect the diffusivity of the liquid may play. This will be in a future report.

B. Literature Articles Pertaining to Corrosive Wear

Baber et al. (5) studied the effect of oxygen in a Ryder gear machine. They took exceptional pains to remove all the oxygen from the system. (They also removed all the moisture, and therefore, did not study the effect of humidity.) The standard Ryder gear procedure was used, which consists of a series of ten-minute steps, each step at a higher load than the preceding step, until 22.5% of the tooth area is scuffed.

With petroleum oils, both with and without antiwear additives, they found a pronounced effect for oxygen. Better performance was always obtained when oxygen was absent. In fact, running in an inert gas gave about the same improvement in scuff load as adding 5% TCP.

They also noted a significant difference in the nature of the surface failure. With air, the failure was predominately scoring or light welding, while with argon there was excessive scuffing and plowing. It appeared that failure in an inert atmosphere required a higher load before it occurred, but once it did occur (as might be expected at the higher load), it was abrupt and severe.

Interestingly, the effect of inert-gas blanketing did not show up with two MIL-L-7808 (ester) oils, nor with two out of three silicone oils.

In a more recent paper (6), the same authors carried out a similar investigation using nitrided gears. These gears are relatively non-corrodible and the results were quite different. Better load-carrying was invariably attained in air than in nitrogen. At higher temperatures, the tests in air showed an additional improved load-carrying capacity -- probably due to oxidation of the oil. In nitrogen, however, higher temperatures gave worse performance -- probably because of the lower viscosity.

Unfortunately, none of the oils run in the first set of experiments were also run in the second, so that an exact comparison cannot be made. Also, none of the oils resemble the relatively high-purity of hydrocarbon fuels so that it is difficult to apply the results to jet fuel problems. However, the importance of metallurgy is clearly shown. In one case, an inert atmosphere is favored; in the other, better results are obtained in air.

Fein and Kreuz (7) used a modified four-ball machine where speeds could be as low as 0.35 rpm and the atmosphere could be controlled by an elaborate seal system. Humidity was not controlled. Runs in air were at ambient humidity, but it may be assumed that in an inert gas the atmosphere was moisture-free. It is not clear whether the runs at intermediate oxygen levels were similarly moisture-free, but the humidity was probably very low. Lubricants were generally highly pure hydrocarbons ranging in viscosity from 0.5 to 1350 cs/100F.

Runs in air showed that paraffinic hydrocarbons gave the highest wear, and aromatics, the lowest. For the low viscosity hydrocarbons of all kinds and for the intermediate-viscosity paraffins, the friction increased rapidly shortly after the start of the test, and the wear rate was high for the remainder of the test. The wear product was α -Fe₂O₃. This behavior was termed "seizure" by the authors. Higher-viscosity oils, including squalane (a paraffin), did not behave in this manner. The authors believed this was because the heavier hydrocarbons dissolve less oxygen. There was also a difference in the wear products, paraffins giving iron oxide, and aromatics giving an amorphous solid.

The effect of oxygen content was quite different with squalane than with cyclohexane vapor. With squalane, the wear rate decreased with decreasing oxygen content for loads of 5 and 20 Kg. At 50 Kg load, however, wear jumped 10-fold when the oxygen content in the air was decreased from 21% to 0.5%. This was attributed to seizure resulting from insufficient oxygen.

With cyclohexane vapor, seizure occurred at high oxygen concentrations and disappeared at low. The authors apparently distinguish between two kinds of

"seizure," one occurring at high oxygen concentrations, the other at low. They believe a "friction polymer" forms on the rubbing surface and that this acts as a heavy viscous liquid, separating the two surfaces. This "friction polymer" forms only at intermediate oxygen levels and is dependent of the hydrocarbon type.

Klaus and coworkers (8 , 9) measured wear rates in the four-ball wear tester for a large number of lubricants of different chemical types. Their tests were mostly at three different temperatures (167 to 310F) and were run in both air and nitrogen. Humidity was not controlled.

A clear effect of temperature was found: in a great majority of cases, wear was higher at higher temperatures. The major exception to this rule was the behavior in air of several of the hydrocarbon lubricants, which gave less wear at higher temperatures. The authors noted that oxidation of the hydrocarbon occurred under these conditions and it seems probable that the oxidized hydrocarbon was acting as an anti-wear agent.

The effect of oxygen was generally to increase wear, although in about one-third of the cases the difference was negligible. Wear was lower in oxygen only for the hydrocarbons at the highest temperature. It is not clear whether this was because of the anti-wear action of the oxidized hydrocarbons, or whether there was an abnormal increase in wear in nitrogen at the highest temperature. If the second, it is not clear whether this is a viscosity effect or whether it is due to the absence of oxygen. The authors favor the latter explanation, partly because they had plotted wear rate against dissolved oxygen, rather than against temperature. The amount of dissolved oxygen was found to decrease with increasing temperature, whereas from Henry's Law it should have been about constant. It appears that the small amount of oxygen dissolved under the nitrogen atmosphere reacted with the hydrocarbon before the analysis could be made. The authors concluded that oxygen is an anti-wear agent in very low concentrations, but their proof is somewhat tenuous.

In the absence of any liquid lubricant, the effect of oxygen is also confusing. Bowden and Tabor (10) stress that an oxide film greatly reduces the "galling tendency" of the surfaces. Tabor (11) points out that "oxygen reduces junction growth and thus is generally beneficial. However, if abrasive wear by hard oxides is serious, rapid oxidation may be accompanied by greatly increased wear." Note that this explanation for the increase of wear in oxygen is different than that of corrosive wear.

Cocks (12) studied high-speed sliding in an unlubricated system and similarly concluded that the presence of oxygen decreased both wear and friction. This was true for steel-on-steel, copper-on-steel, and nickel-on-nickel. Glaeser (13) investigated AISI 52100 steel ball bearings both lubricated and dry. When dry, the bearings failed rapidly in an inert atmosphere. When flooded with oil, they were about equivalent in air and inert atmospheres. This makes cooling appear to be the important contribution of the lubricant.

However, Begelinger and deGee (14), studying silver-on-steel, found that oxygen increased both wear and friction. They concluded that the wear mechanism changed from mild abrasive to severe adhesive and that this was due to a reaction between the oxygen and the iron surface. The iron oxide so formed is postulated to increase the adhesion between the iron and silver. This latter behavior appears to be very similar to lubricated results with steel-on-steel.

This review of the literature on the effect of inerting a lubrication system shows the extent of the disagreement in both the data and the interpretation of the data. Whether oxygen and water vapor are helpful or harmful depends on the specific metallurgy, the lubricant, and the operating conditions.

III. EXPERIMENTAL WORK

The experimental work reported herein falls into three groups. First, a number of different hydrocarbons were evaluated in lubricity to see how they behaved in their pure state. Second, the effect of oxidation on lubricity was examined. Third, additional data were obtained to try to explain the unusual behavior of 1-methyl naphthalene in lubricity. Finally, data are presented on the effect of anti-icing additive on friction and wear.

A. Effect of Hydrocarbon Type in Various Environments

It has been found that for paraffinic fuels friction and wear of steel-on-steel are higher in air than in argon but a heavy aromatic (1-methyl naphthalene) gives much higher wear and friction in argon. Evidently, the effect of atmosphere on lubricity is dependent upon the hydrocarbon type. A large number of hydrocarbons including paraffins, olefins, naphthenes, and aromatics were therefore tested in the ball-on-cylinder device to see if there is a certain pattern correlating the molecular structure with lubricity. The test work covered in this report were carried out by testing these hydrocarbons individually. The effect of their blending with the jet fuel will be investigated and reported subsequently.

1. Light Hydrocarbons

Six hydrocarbons, as shown in Table 1, were selected to represent six different chemical structures: paraffin, isoparaffin, naphthene, alkyl naphthene, aromatic, and alkyl aromatic. These hydrocarbons were chromatographic grade reagent, having a viscosity of about 0.7 cs which simulates the viscosity of jet fuels at about 200F. These tests were made at room temperature and in various atmospheres. The results indicate that these light hydrocarbons, regardless of their molecular structure, give the highest wear in wet air, high wear in dry air, and the lowest wear in argon. No anomalous phenomenon was observed in testing these aliphatic one-ring hydrocarbons.

2. Two-Ring Hydrocarbons

Table 2 shows the results from ball-on-cylinder tests on various two-ring hydrocarbons. These hydrocarbons represent three different types of polynuclear compounds with various degrees of unsaturation. In the first group, both rings are saturated; in the second group, one ring is saturated, the other aromatic; in the third group, both rings are aromatic. Among all these hydrocarbons, only indene showed the same lubricating characteristics as 1-methyl naphthalene, giving higher friction and wear in argon than in air.

It was also noted that these two-ring hydrocarbons generally gave lower wear in both dry air and wet air than Bayol 35, a highly refined paraffinic fuel. (The wear scar under the same test conditions for Bayol 35 is about 0.55 mm in dry air and 0.70 mm in wet air.) These results suggest that corrosive wear may be less in these polynuclear aromatics than in paraffins of similar viscosity. However, the hydrocarbons used in these tests were technical grade reagent with a purity of >95%. It is not certain whether the observed effectiveness is simply due to the presence of certain impurities. Some of these hydrocarbons will therefore be purified for more tests for further confirmation.

TABLE 1

EFFECT OF HYDROCARBON TYPE

(Ball-On-Cylinder Tests, Steel-On-Steel; 240 g Load, 240 rpm, 32 Min, 80°F)


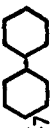



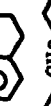
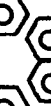


Cylinder No.	Hydrocarbons	Vis. cs @ 77°F	Coefficient of Friction				Wear Scar, mm		
			Argon	Dry Air	Wet Air	Argon	Dry Air	Wet Air	Wet Air
203	n-Octane	0.74	0.13	0.20	0.20	0.21	0.45	0.74	
356	2,2,4 Trimethyl-pentane	0.69	0.13	0.26	0.22*	0.23	0.76	0.85	
203	Cyclohexane	1.13	0.12	0.20	0.20*	0.19	0.74	0.82	
203	Methylcyclopentane	0.61	0.13	0.25	0.55*	0.25	0.73	0.92	
203	Benzene	0.68	0.15	0.19	0.23*	0.23	0.52	0.92	
203	Toluene	0.63	0.12	0.16	0.23*	0.22	0.49	0.85	

* Friction trace erratic.

TABLE 2

EFFECT OF TWO-RING HYDROCARBONS

(Ball-On-Cylinder Tests, Steel-On-Steel, 1000 gm Load, 240 rpm, 32 Min, 80°F)

Cylinder No.	Hydrocarbons	Molecular Formula	Vis. cs @ 77°F	Coefficient of Friction			Wear Scar, mm		
				Argon	Dry Air	Wet Air	Argon	Dry Air	Wet Air
330	Decalin		2.87	0.12	0.14	0.16*	0.26	0.35	0.42
295	Isopropyl-bicyclohexyl _{C₃H₇}		9.46	0.11	0.11	0.10	0.24	0.24	0.35
303	Dimethano-decalin		11.50	0.11	0.11	0.10	0.21	0.29	0.41
330	Phenyl-cyclohexane		2.70	0.13	0.14	0.16	0.31	0.33	0.50
303	Tetralin		2.10	0.13	0.16	0.19	0.25	0.42	0.68
303	Indane		1.52	0.13	0.13	0.17	0.30	0.31	0.42
323	Diphenyl-methane		2.90	0.12	0.12	0.17	0.29	0.43	0.62
303	Methyl-naphthalene		2.65	0.17	0.11	0.13	0.82	0.33	0.36
323	Indene		1.71	**	0.15*	0.14	0.93 (1.05)	0.72 (0.90)	0.33 (0.35)

* Friction trace erratic.

3. Olefins

Ball-on-cylinder tests were made on various olefins, including aliphatic alkenes, cycloalkenes, and olefinic aromatics. The results are presented in Table 3. In dry air, as shown in Figure 3, the alkenes gave less wear than the alkanes, but in wet air there was no appreciable difference. A direct comparison of wear for the corresponding pairs is shown below:

Hydrocarbon	Wear Scar, mm		
	Argon	Dry Air	Wet Air
Octane	0.21	0.62	0.74
Octene-1	0.19	0.33	0.86
Cyclohexane	0.24	0.73	0.79
Cyclohexene	0.31	0.31	0.75
2,2,4-Trimethyl-pentane	0.23	0.76	0.85
2,5-Dimethyl-1,5-hexadiene	0.23	0.25	0.94

Cyclohexane, despite its higher viscosity, gave higher wear in air than cyclohexene.

Figure 3 also shows that olefinic cycloalkenes give less wear not only in dry air but also in wet air. It is noteworthy that bicyclo-(2,2,1)-heptadi(2,5)ene and methyl styrene gave less wear in both dry and wet air than aliphatic alkanes and alkenes, despite their tests at a much higher load (1000 gm vs 240 gm). This indicates the chemical structure of the unsaturated groups may be important for reduction of corrosive wear.

It is known that olefinic hydrocarbons are more readily oxidized than paraffinic hydrocarbons and their oxidation rates are dependent upon the bond structure. According to the published data of oxidation rates for some hydrocarbons (refer to Scott, G., "Atmospheric Oxidation and Antioxidants," Elsevier Publishing Company, Amsterdam, 1965), the relative molar rate for α -methyl styrene and octene-1 is 200:2.4. It seems that the difference in reactivity towards oxygen may be a contributing factor for their difference in reducing the corrosive wear. The relative oxidation rates for these hydrocarbons were estimated by Boland's empirical rule (refer to Boland, J. L., Trans. Faraday Soc., 46, 1950) and are shown below together with some published experimental data:

Hydrocarbon	Relative Oxidation Rate ⁽¹⁾		Wear Scar Diameter, mm @ 240 g in Wet Air
	Calculated	Experimental	
Octene-1	1	1	0.86
2-5 Dimethyl-1,5-hexadiene	2.6	2.5*	0.94
Cyclohexene	11.1	10.3	0.75
4-Vinyl-cyclohexene	350	--	0.32
Bicyclo(2,2,1)-heptadi(2,5)ene	1160	--	0.47 (0.39)**
α -Methyl-styrene	--	83	0.44**
Alkane (n-decane)	--	0.1	--

(1) From G. Scott (See text).

* Experimental data for diallyl.

** Wear at 1000 g load.

TABLE 3

EFFECT OF OLEFINIC HYDROCARBONS

(Ball-On-Cylinder Tests, Steel-On-Steel, 240 rpm, 32 Min, 77°F)

Cylinder No.	Hydrocarbons	Vis. cs @ 77°F	Load gm	Coefficient of Friction			Wear Scar, mm		
				Argon	Dry Air	Wet Air	Argon	Dry Air	Wet Air
181	n-Octane	0.74	240	0.13	0.20	0.20*	0.21	0.62	0.74
181	2,2,4 Trimethyl-pentane	0.69	240	0.13	0.26*	0.22*	0.23	0.76	0.85
213	Cyclohexane	1.13	240	0.13	0.22	0.20*	0.24	0.73	0.79
181	Octene-1	0.66	240	0.13	0.18	0.22*	0.19	0.33	0.86
181	2,5 Dimethyl-1,5-hexadiene	0.63	240	0.13	0.16	0.27*	0.23	0.25	0.94
213	Cyclohexene	0.76	240	0.22	0.23	0.22*	0.31	0.31	0.75
323	Bicyclo(2,2,1)heptadi(2,5)ene	0.93	240	0.15	0.16	0.18*	0.25	0.38	0.47
213	4-Vinyl cyclohexene	0.79	240	0.11	0.12	0.19*	0.18	0.19	0.32
234	Bicyclo(2,2,1)heptadi(2,5)ene	0.93	1000	0.21*	0.19*	0.13*	0.24	0.40	0.39
234	Ar-Methyl styrene	0.95	1000	0.15*	0.14*	0.18*	0.28	0.28	0.44
234	Ar-Methyl styrene	0.87	1000	0.14	0.11	0.17*	0.42	0.25	0.44

* Friction trace erratic.

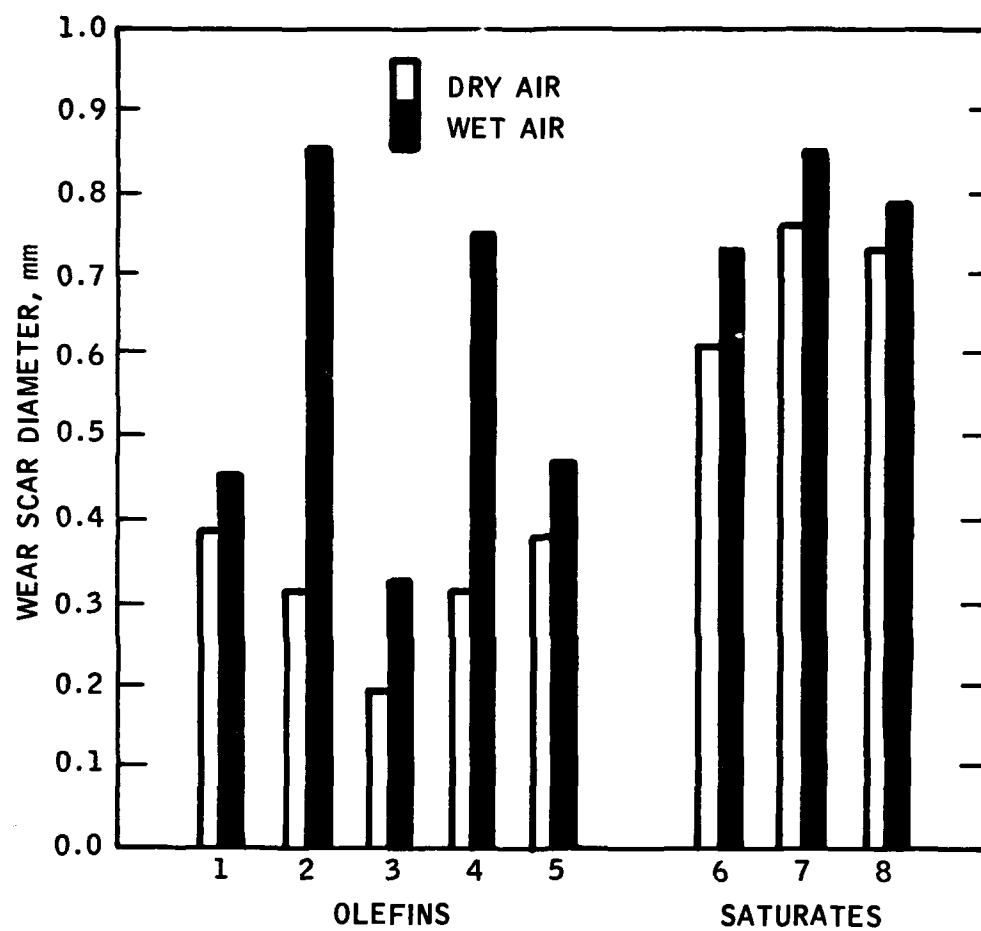


FIGURE 3

WEAR IN DRY AIR AND WET AIR FOR LIGHT HYDROCARBONS

Note that the olefins that have the highest oxidation rate are the more effective in reducing corrosive wear. It is conceivable that there may be less corrosive wear in hydrocarbons having higher oxidative reactivity, because of either their competitive reaction with oxygen to ease the oxygen attack to the metal surface, more probably, or the formation of polar components in oxidation for wear protection. This phenomenon will be further investigated.

B. Effect of Oxidation on the
Lubricity of Fuels

Previous test results at temperatures below 160F indicated that oxygen attack on the metal surface rather than oxidation of the fuel played the major role in friction and wear. When the fuels were tested at a higher temperature, 240F, the oxidized components in fuels gave wear protection, as observed in Vickers vane pump tests and confirmed in ball-on-cylinder tests. The oxidation was found to be dependent upon the temperature and time as identified by thin layer chromatography and acidity determinations.

1. PW-523 Gave Lower Pump Wear
Than Bayol 35 in Air at 240F

Vickers vane pump tests were made at 240F in various atmospheres on several commercial fuels. The test data are shown in Table 4. In an inert atmosphere, wear was again reduced to a very low level. However, in air the highly-refined fuels again gave more severe wear than the other commercial fuels. The severity of wear for highly-refined fuels was even higher in wet air. This is in agreement with the results from the ball-on-cylinder tests, indicating that the wear is of the corrosive type. It was rather unexpected that PW-523 gave less wear than Bayol 35 at 240F in both dry air and wet air, inasmuch as they showed the same severity of wear at a lower temperature. It was then speculated that the oxidation of fuels at higher temperatures might become a significant factor to account for such a difference.

2. Oxidation of PW-523 at 240F
Was Indicated by Oxidation Tests

A series of oxidation tests was therefore made on PW-523 and Bayol 35. These tests were carried out by heating the fuels to 240F or 400F in nitrogen. After the temperature became steady, air was introduced to replace nitrogen. Samples were taken at time intervals of one hour, two hours, and four hours, and were cooled in nitrogen. These oxidized fuel samples were used for ball-on-cylinder tests and chemical analyses. The test results are shown in Table 5. An increase of acidity for PW-523 was detected after its being oxidized at 240F for one hour and this was accompanied by a decrease in wear. As shown in Figure 4, the decrease of wear is a close function of the increase of oxidation time. A difference in acidity for Bayol 35 was not detectable after oxidation at 240F for 4 hours. The wear decreased slowly with the increase of oxidation time as shown in Figure 5. At 400F both fuels were oxidized rapidly and the wear was consistently at a low level. The Neut. No. may be considered representative of the extent of oxidation. A plot of wear versus Neut. No. is shown for PW-523 in Figure 6. It appears that a low severity of wear may be attained at a Neut. No. of about 100 ppm KOH. This is in surprisingly good agreement with previous tests that had shown that about 30 ppm of oleic acid was equally effective.

TABLE 4
VICKERS VANE PUMP TESTS
(Sump Temperature, 240°F)

	Rayol-35				FM-523				JP-5				RAP-176-64				RAP-173-61			
	N ₂	Dry Air	Wet Air		N ₂	Dry Air	Wet Air		N ₂	Dry Air	Wet Air		N ₂	Dry Air	Wet Air		N ₂	Dry Air		
Pressure, psig	150	145	150		148	150	150		125	130	130		145	155	150		125	120		
Pumping Rate, gpm	0.49	0.23	0.28		0.42	0.44	0.49		0.30	0.39	0.38		0.47	0.29	0.44		0.27	0.28		
Vol Eff., %	27	13	16		23	24	27		17	22	21		26	16	24		15	16		
Wear, mg																				
Wt Loss of Vanes	1	80	162		1	58	70		2	3	5		1	3	5		1	8		
Wt Loss of Ring	23	1851	2941		78	180	239		64	15	17		63	64	46		17	441		
Surface Roughness																				
Vaness, Initial	20	19	24		17	20	18		21	22	14		21	20	26		21	21		
Vaness, Final	31	>200	>200		24	>200	76		19	22	15		26	11	26		34	22		
Ring, Initial	12	8	12		15	10	10		19	12	11		10	12	18		11	14		
Ring, Final	7	>200	>200		12	40	29		10	13	11		18	15	9		9	10		

* Run stopped at 12 hours due to a leakage in the system.

TABLE 5

EFFECT OF OXIDATION OF FUELS

{Ball-On-Cylinder Tests, Steel-On-Steel, 1000 g Load,
240 rpm, 32 Min, Open Air, 80°F}

<u>Fuel</u>	<u>Oxidation</u>		<u>Acidity, ppm/KOH</u>	<u>Coeff. of Friction</u>	<u>Wear Scar Diameter mm</u>
	<u>Temp °F</u>	<u>Time Hr</u>			
PW-523	-	0	< 0.2	0.20*	0.71
PW-523	240	1	0.55	0.20	0.52
PW-523	240	2	0.77	0.22	0.48
PW-523	240	4	3.75	0.19	0.36
PW-523	240	24	32.6	0.19	0.32
PW-523	400	1	37.2	0.19	0.30
PW-523	400	2	130.1	0.18	0.26
PW-523	400	4	960.0	0.18	0.28
PW-523	-	0	< 0.2	0.19*	0.64
Bayol 35	-	0	< 0.2	0.22*	0.80
Bayol 35	240	1	< 0.2	0.22*	0.80
Bayol 35	240	2	< 0.2	0.21*	0.75
Bayol 35	240	4	< 0.2	0.21*	0.66
Bayol 35	240	24	85.5	0.19	0.36
Bayol 35	400	1	80.0	0.19	0.32
Bayol 35	400	2	172.9	0.17	0.27
Bayol 35	400	4	785.0	0.16	0.26
Bayol 35	-	0	< 0.2	0.21*	0.80

* Friction trace erratic.

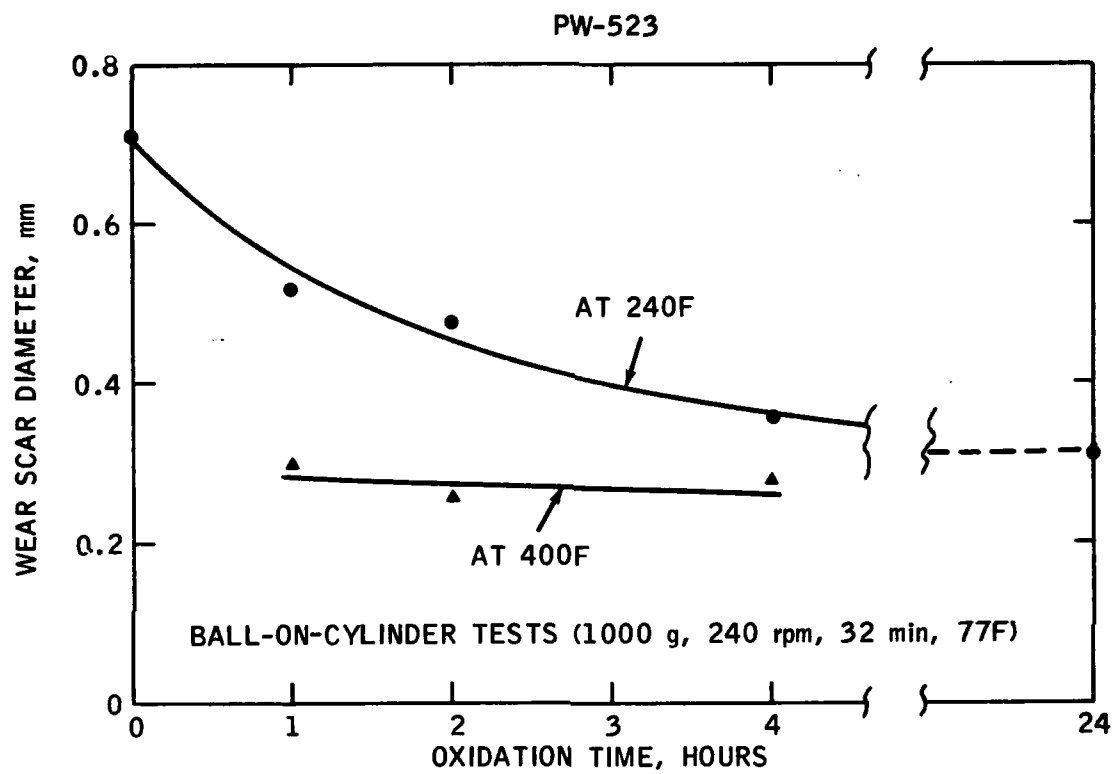


FIGURE 4

WEAR VERSUS OXIDATION TIME FOR PW-523 AT 240F AND 400F

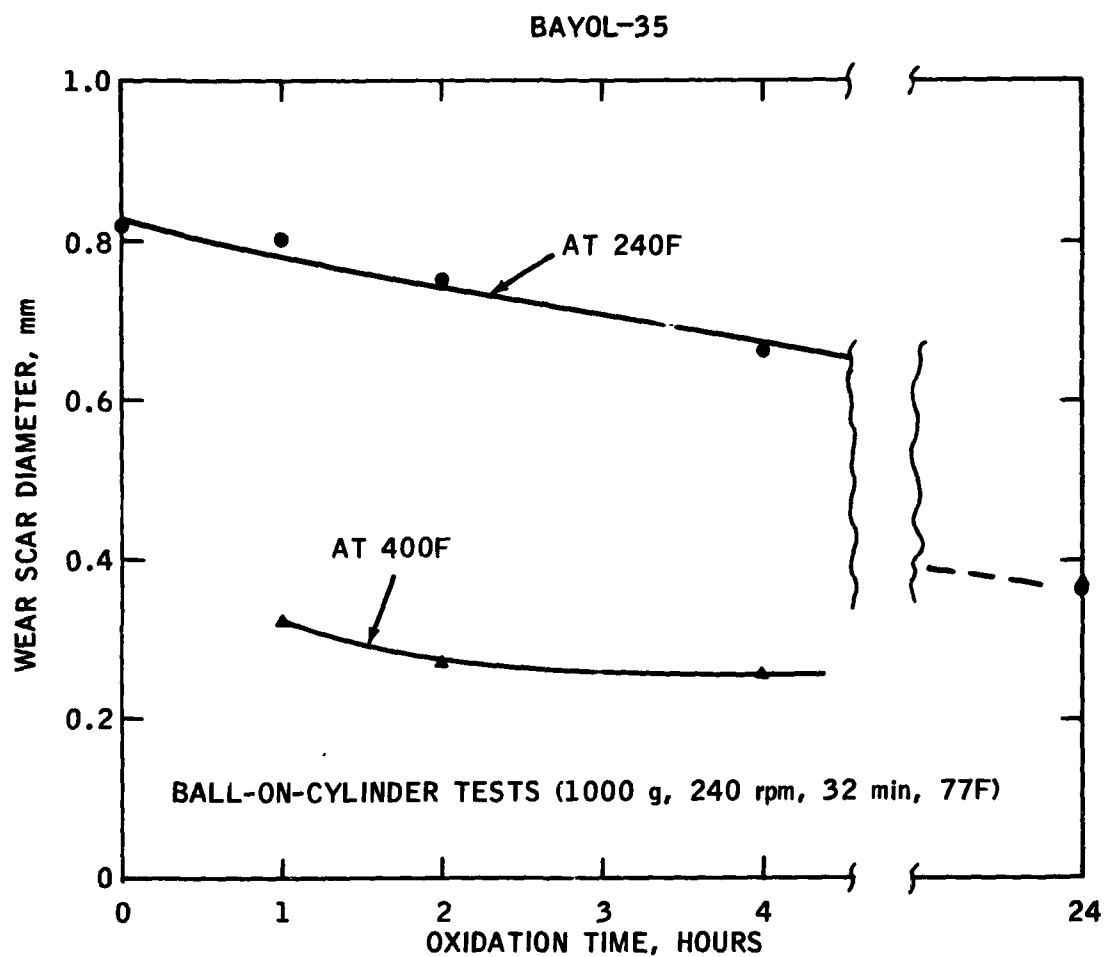


FIGURE 5

WEAR VERSUS OXIDATION TIME FOR BAYOL 35 AT 240F AND 400F

PW-523 AFTER OXIDATION

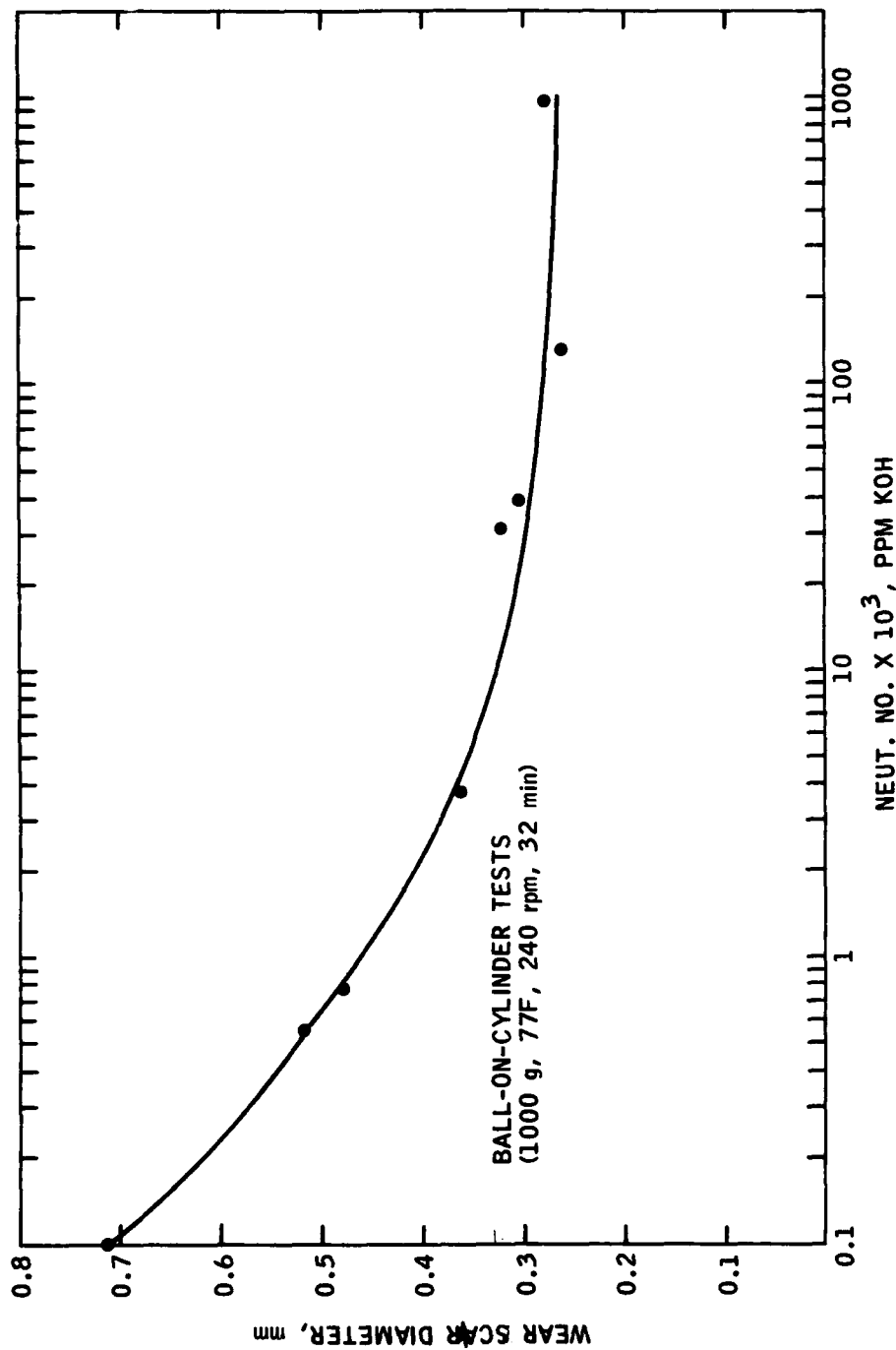


FIGURE 6

WEAR VERSUS NEUT. NO. FOR PW-523 AFTER OXIDATION

Ball-on-cylinder tests were also made on other commercial fuels before and after 24-hour pump tests at 240F. The results are shown in Table 6. It is clearly seen that the highly-refined fuels were more oxidized than the other commercial fuels and the extent of the wear reduction was correspondingly greater.

3. Thin Layer Chromatography Indicates the Formation of Polar Components in Oxidation

For investigating the chemical change in oxidation, thin layer chromatography was used to examine the fuels. Thin layer chromatography is essentially a type of adsorption chromatography where the absorbent is a thin layer of a solid, such as silica gel, deposited on a plate support. The sample to be analyzed is placed near one end of the plate and is resolved by a solvent (developer) passing through the layer by capillary action. The trace components are adsorbed at different spots and can be made visible by a treatment with certain indicators.

Figure 7 shows the thin layer chromatogram for these commercial fuels before and after pump tests at 240F. These analyses were carried out using 5 μ l sample of a solution of 10% fuel in pentane. Isooctane was used as the developer; phospho-molybdic acid as the indicator. It shows clearly that a new polar component was produced in oxidation for all the highly-refined fuels. For other commercial fuels, the polar component was present originally and was only slightly increased.

The sample of PW-523 from oxidation tests at 240F and 400F were also analyzed by thin layer chromatography as shown in Figure 8. The size and intensity of these polar spots increased distinctly with temperature and oxidation time. The quantitative evaluation of the chromatogram by a densitometer was tried. For samples oxidized at 400F, the intensity ratio of these spots for one hour, two hours, and four hours was approximately 1:2:5. For further identification of these polar components, a large sample was prepared on the thin layer plate and the adsorbed spots were removed from the plate and dissolved in methanol. This sample will be analyzed by IR, GC, and mas spectroscopy.

4. Oxidation Rather Than Thermal Decomposition Is Contributing Factor to Lubricity

To confirm that it was an oxidative change and not merely thermal decomposition that caused the improved lubricity, ball-on-cylinder tests were made on Bayol 35 which had been heated at 400F in nitrogen or in air for 2 hours. The results are shown in Table 7. It is obvious that heating alone did not have any appreciable effect to the fuel lubricity. The chemical change of fuels, which showed the effectiveness on friction and wear, is clearly oxidation.

None of these findings is in any sense surprising. Oxidized hydrocarbons are known to be good lubricity agents and these tests have merely confirmed this fact. The data do point out that the effect of temperature can be easily masked if oxidation is occurring simultaneously and that differences between hydrocarbons may be more a difference in oxidative stability rather than a difference in native lubricity.

TABLE 6

FUELS AFTER PUMP TEST AT 240°F IN OPEN AIR

(Ball-On-Cylinder Tests, Steel-On-Steel, 1000 g, 240 rpm, 32 Min, 77°F)

<u>Fuel</u>	<u>Vis. cp @ 77°F</u>	<u>Neut. No. ppm KOH</u>	<u>Coef. of Friction</u>	<u>Wear Scar mm</u>
Bayol-35				
Before Pump Test	2.416	< 0.2	*	0.62
After Pump Test	2.376	85.5	0.14	0.35
RAF-173-61				
Before Pump Test	2.151	0.3	0.18	0.54
After Pump Test	2.063	48.7	0.15	0.28
FW-523				
Before Pump Test	1.513	< 0.2	0.16	0.63
After Pump Test	1.510	37.9	0.16	0.35
JP-5				
Before Pump Test	1.466	0.8	0.21	0.45
After Pump Test	1.461	9.7	0.15	0.28
RAF-176-64				
Before Pump Test	1.310	9.5	0.17	0.29
After Pump Test	1.336	13.8	0.16	0.28

* Run stopped at 14 min because of excessive friction.

THIN LAYER CHROMATOGRAM



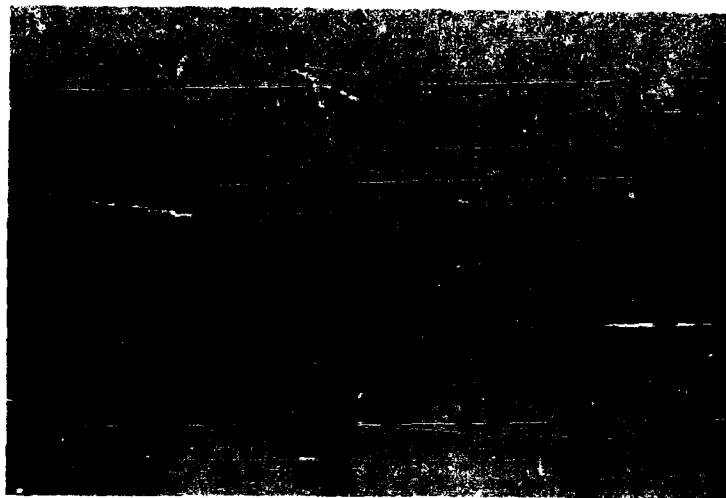
b a b a b a b a b a
PW-523 Bayol 35 JP-5 RAF-173 RAF-176

SOLUTION; 10% FUEL IN PENTANE
SAMPLE SIZE: 5 μ l
DEVELOPER: ISOOCANE
INDICATOR: PHOSPHOMOLYBDIC ACID

FIGURE 7

THIN LAYER CHROMATOGRAM OF FUELS BEFORE AND AFTER OXIDATION

PW-523
THIN LAYER CHROMATOGRAM



400F 240F 240F 240F 400F 400F 400F
1 Hr. 1Hr. 2 Hr. 4 Hr. 1 Hr. 2 Hr. 4 Hr.

SOLUTION: 10% IN PENTANE
SAMPLE SIZE: 5 μ l
DEVELOPER: ISOCTANE
INDICATOR: PHOSPHOMOLYBDIC ACID

FIGURE 8

THIN LAYER CHROMATOGRAM FOR PW-523 AFTER OXIDATION

C. Mechanism Studies on 1-Methyl Naphthalene

The data presented in previous reports, and confirmed in this report, show that 1-methyl naphthalene is an unusual hydrocarbon. Other hydrocarbons give the highest wear in wet air and are responsive to the presence of oxidized hydrocarbons and corrosion inhibitors such as oleic acid. This clearly is corrosive wear, in which FeO is the wear product. 1-Methyl naphthalene behaves quite differently, giving the highest wear in a dry inert atmosphere and being unaffected by oxidation or lubricity additives. Its wear product is Fe.

Of all the other hydrocarbons only indene behaved similarly. Other aromatics and cyclic naphthenes do not show this behavior. Furthermore, and even more perplexing, 1-methyl naphthalene is a good lubricity component in paraffinic fuels, both in argon and air. It shows marked synergism in both atmospheres. Learning more about the behavior of this hydrocarbon may give important clues to the behavior of other hydrocarbons in systems where corrosive wear is not possible, as for example in stainless steel.

The high wear of 1-methyl naphthalene in argon does not appear to be due to any unusual purity. In fact, as reported earlier, the first sample of 1-methyl naphthalene tested actually contained about 40% 2-methyl naphthalene. Nor does it require an unusual degree of oxygen-exclusion. To the contrary, the effect persists even in atmospheres having as much as 1% oxygen. Under these conditions, the amount of oxygen dissolved is about 1 ppm, which is nearly 100 times more than that dissolved in Bayol 35 under argon. Figure 9 shows how the wear decreases sharply when more than 1 ppm oxygen is present. Data are presented in Table 8.

The effect of oxygen is apparently directly on the metal surface, acting in a manner similar to water to decrease the adhesion between the two metal surfaces. It does not act by changing the hydrocarbon itself, or if it does, it is by an unusual catalytic reaction at the surface. Table 9 presents data on the effect of first oxidizing 1-methyl naphthalene in air and then running a ball-on-cylinder test on the oxidized sample. After 1 hour at 400F, considerable oxidation had taken place, as evidenced by the increase in acidity and the appearance of polar compounds in TLC. However, these compounds had no effect on lubricity. This is in agreement with the effect of oleic acid, which also did not improve the lubricity of 1-methyl naphthalene in argon. The thin layer chromatogram for 1-methyl naphthalene before and after oxidation is shown in Figure 10.

Another possibility was that 1-methyl naphthalene in argon was undergoing scuffing, even though the loads were relatively low. To investigate this, 4-ball wear tests were run at several loads. Figure 11 shows the results. The usual scuffing case is typified by cetane in air: wear is low at low loads and then increases suddenly and catastrophically when the transition load is reached. 1-Methyl naphthalene does not show this behavior, but merely increases its wear rate continuously with load. It is possible that 1-methyl naphthalene scuffs at very low loads, and that all these tests were under scuffing conditions. This will be investigated further. However, this is not an explanation but merely a manifestation of its unusual behavior.

Finally, a comparison was made between 1-methyl naphthalene and an unlubricated system. It was felt that 1-methyl naphthalene was possibly behaving as if no lubricant at all were present. The unlubricated system was tested under the four conditions of wet and dry argon, and wet and dry air. Data are given in Table 10. Like 1-methyl naphthalene, it gave high wear and high friction in dry

TABLE 7

EFFECT OF OXIDATIVE AND THERMAL STABILITY

(Ball-On-Cylinder Tests - Bayol-35, 1000 g, 77°F, 240 rpm, 32 Min)

	<u>No Heating</u>	<u>Heated @ 400°F in Argon</u>	<u>Heated @ 400°F in Air</u>
Vis. @ 77°F, cs.	3.079	3.060	3.144
Neut. No. ppm KOH	< 0.3	< 0.3	394
New Compounds in TLC	0	0	1

Ball-On-Cylinder Tests

● Coeff. of Friction

in Argon	0.12	0.12	0.12
in Dry Air	0.14	0.13	0.11
in Wet Air	0.16*	0.14*	0.11

● Wear Scar, mm

in Argon	0.26	0.22	0.23
in Dry Air	0.56	0.53	0.27
in Wet Air	0.70	0.72	0.41

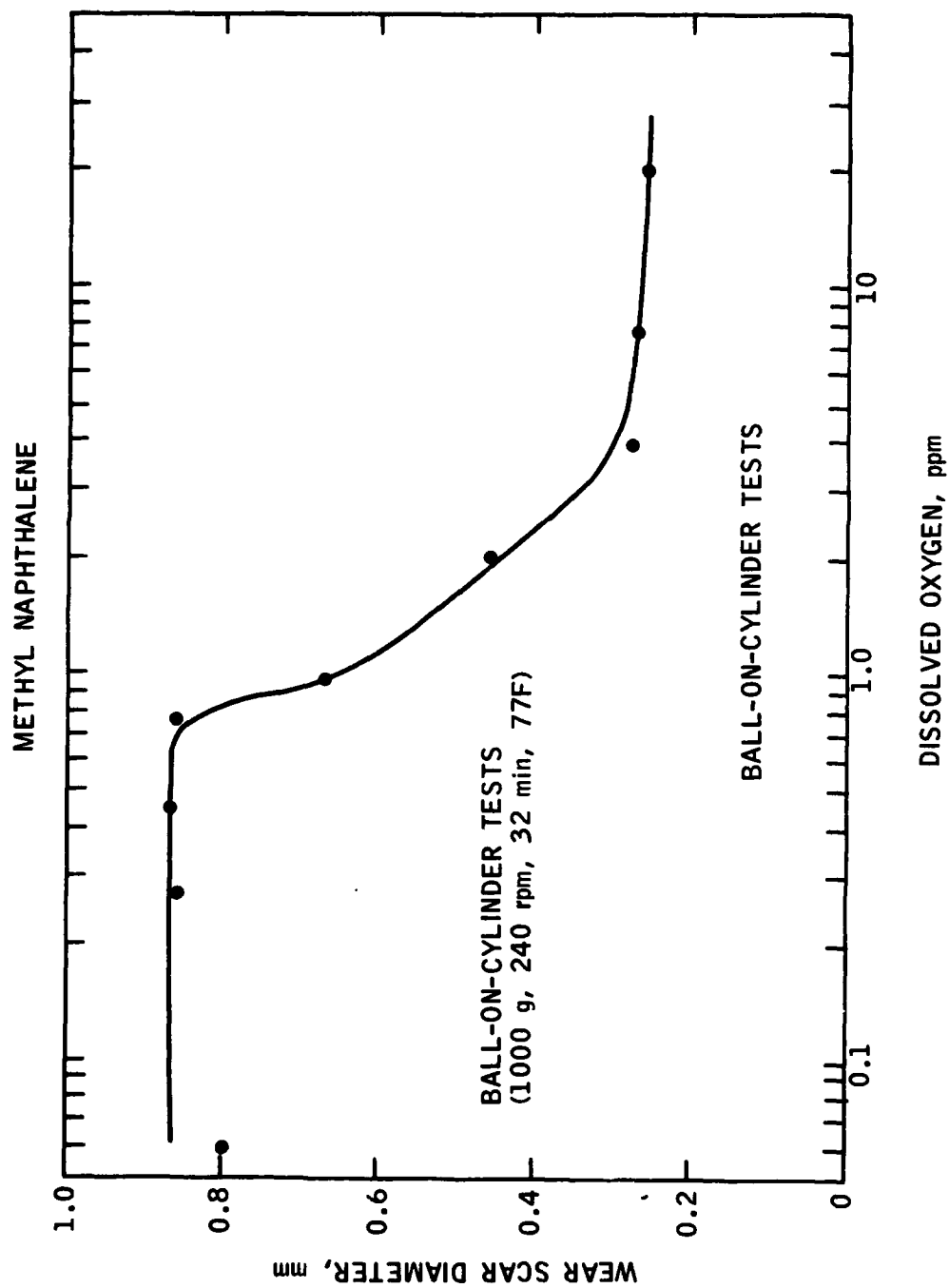


FIGURE 9
THE EFFECT OF DISSOLVED OXYGEN ON WEAR FOR 1-METHYL NAPHTHALENE

TABLE 8

EFFECT OF DISSOLVED OXYGEN IN METHYL NAPHTHELENE

(Ball-On-Cylinder Tests, 100 gm, 80°F, 240 rpm, 32 Min)

<u>Atmosphere</u> <u>% O₂</u>	<u>O₂ in Fuel</u> <u>ppm</u>	<u>Wear Scar Diameter</u> <u>mm</u>	<u>Coefficient of Friction</u>
0.06	0.06	0.80	0.10*
0.28	0.27	0.86	0.13*
0.52	0.50	0.87	0.17*
0.76	0.72	0.86	0.11*
1.02	0.96	0.67	0.11*
2.10	2.00	0.46	0.11
4.13	3.94	0.28	0.11
8.00	7.60	0.27	0.11
21.00 (Dry Air)	20.00	0.26	0.11

* Friction trace erratic.

TABLE 9
EFFECT OF THERMAL AND OXIDATIVE STABILITY

(Methyl Naphthalene)

	<u>No Heating</u>	<u>After Heated At 400°F in Argon</u>	<u>After Heated At 400°F in Air</u>
Vis. @ 77°F, cs	2.628	2.636	2.764
Neut. No. x 10 ³ , ppm KOH/gm	7.0	8.8	314.7
New Components in *TLC	0	0	3
<u>**Ball-On-Cylinder Tests:</u>			
Coeff. of Friction			
in Argon	0.14	0.13	0.08
in Dry Air	0.10	0.09	0.09
in Wet Air	0.14	0.12	0.10
Wear Scar, mm			
in Argon	0.70	0.73	0.75
in Dry Air	0.35	0.40	0.49
in Wet Air	0.43	0.41	0.35
% Metallic Contact			
in Argon	100	100	100
in Dry Air	98.3	86.4	76.8
in Wet Air	100	100	100

* Thin-Layer Chromagraph

** 1000 gm Load, 240 rpm, 80°F, 32 Min

THIN LAYER CHROMATOGRAM

(1)	(2)	(3)
NO	400°F	METHANOL
TREATMENT	IN AIR	EXTRACT
		OF (2)

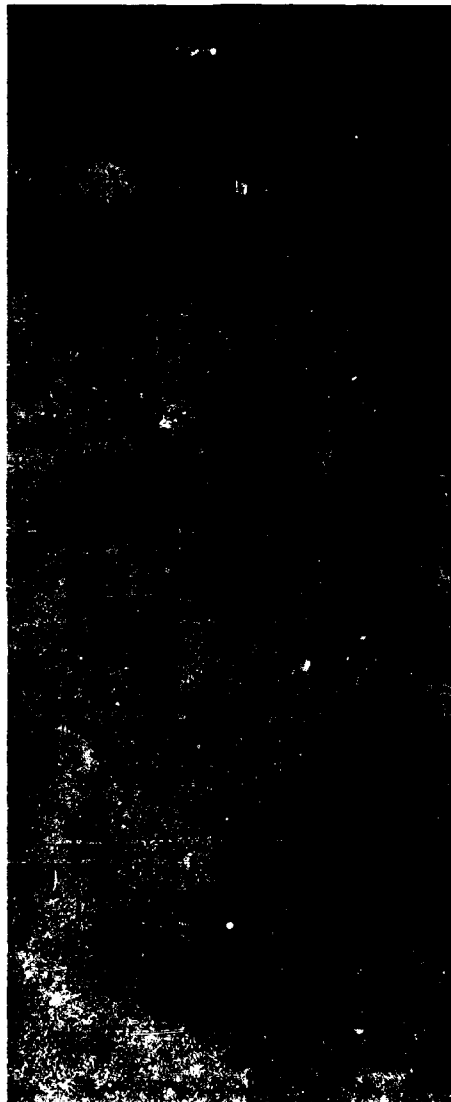


FIGURE 10

THIN LAYER CHROMATOGRAM FOR 1-METHYL NAPHTHALENE
BEFORE AND AFTER OXIDATION AT 400F

FOUR-BALL WEAR TESTS

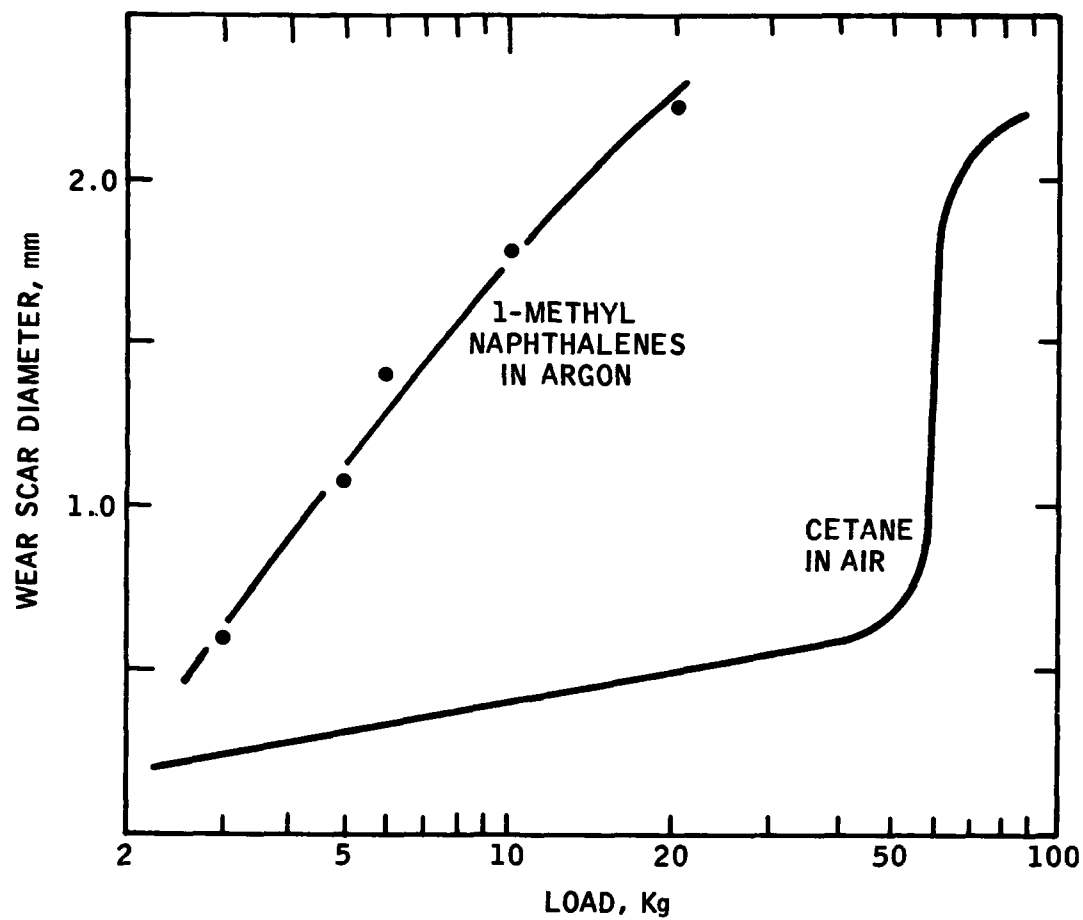


FIGURE 11
COMPARISON OF SCUFFING OF CETANE IN AIR
AND WEAR OF METHYL NAPHTHALENE IN ARGON

argon and much lower wear and friction in wet argon. This gives some confirmation that in argon 1-methyl naphthalene is simply no lubricant at all. However, this would mean that all other hydrocarbons (even heptane or benzene, as shown in Table 10) are somehow acting as good lubricity agents in argon -- a concept that is just as hard to believe. Furthermore, in the presence of oxygen, there is no resemblance between the unlubricated system and 1-methyl naphthalene. The wear scars were high in both wet and dry air, being somewhat higher in wet. This behavior is similar to the behavior of most other hydrocarbons, and just the opposite of 1-methylnaphthalene. Thus, the unlubricated system resembles 1-methyl-naphthalene in argon and other hydrocarbons in air.

The friction level and the appearance of the wear scar gives some indication of the kind of wear occurring when no lubricant is present. Photomicrographs of the wear scars are shown in Figure 12. In wet air, the scar is very large (1.07 mm) and smooth, and the friction is low (0.29). Oxygen and water vapor are adsorbing on the rubbing surface, preventing adhesion, but causing corrosive wear with the formation of iron oxide. The iron oxide may also be acting as a mild abrasive, although if so, it is not contributing much to the friction.

In dry air, the wear is again high (0.91 mm) but this time it is accompanied by high friction (0.75). The wear scar shows the presence of a wear fragment adhering to the surface. There is obviously some adhesion and metal transfer going on in the absence of water, and this is responsible for the higher friction.

In dry argon, the results are almost the same as in dry air. Wear is high (0.95) and friction is even higher (1.32). The absence of oxygen has made adhesion more severe, and the rough wear scar attests to this. Both heptane and benzene greatly reduce this adhesion, but 1-methyl naphthalene does not.

In wet argon, wear is at its lowest level (0.25 mm) but friction is higher than in wet air. The water reduces adhesion somewhat, although not as effectively as water plus oxygen. However, corrosive wear does not occur, hence wear is low.

D. Effect of Anti-Icing Additive (AIA) on Lubricity

Anti-icing additive is used in jet fuels to lower the freezing point of any suspended water. It consists of 99.6% Cellosolve (methyl ester of ethylene glycol) and 0.4% glycerine; it is used in 0.1% concentration in jet fuel.

An evaluation of fuels containing AIA was made in the ball-on-cylinder device. It appears that AIA is quite sensitive to humidity although for the most part it does not have much of an effect on either friction or wear. In general, AIA acts as a lubricity agent (although not a very good one) in dry air, reducing both friction and wear. In wet air, however, it merely accentuates the effect of water. Water itself, as has been shown before, accelerates corrosive wear giving higher friction and wear. AIA helps dissolve more water and therefore gives still more friction and wear. At low humidities then, AIA is somewhat beneficial while at high humidities it is somewhat detrimental.

Table 11 presents two sets of ball-on-cylinder tests; one with isooctane as a base fuel, the other with Bayol 35. It can be seen that AIA has an anti-wear effect in the absence of water and a pro-wear effect in the presence of water. AIA gives a 50% reduction in wear scar diameter in dry air (10-15 fold reduction

TABLE 10
EFFECT OF OXYGEN AND MOISTURE

Ball-on-Cylinder Tests (240 g, 32 Min., 81F)

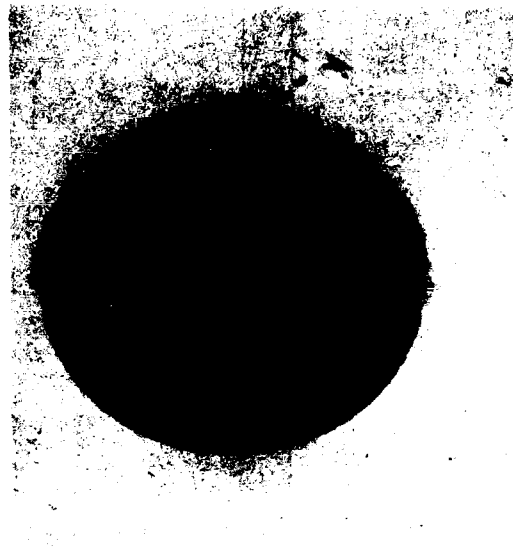
Atmosphere	Lubricant:	Coefficient of Friction				Wear Scar Diameter, mm		
		None	Heptane	Benzene	1-Methyl Naphthalene*	None	Heptane	Benzene 1-Methyl Naphthalene*
Dry Air		0.75	0.29	0.22	0.11	0.91	0.42	0.24 0.33
Wet Air		0.29	0.28	0.38	0.12	1.07	0.89	0.95 0.36
Dry Argon		1.32 (1.35)	0.26	0.18	0.16	0.95 (0.82)	0.27	0.17 0.70
Wet Argon		0.57 (0.69)	0.23	0.32	---	0.25 (0.52)	0.24	0.12 ---

Data in the parentheses are those from duplicate runs.

* Tests at 1 Kg load.



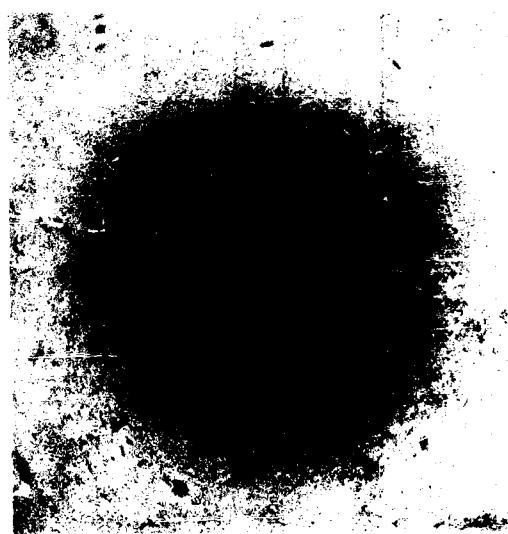
IN DRY AIR



IN WET AIR



IN DRY ARGON



IN WET ARGON

FIGURE 12

PHOTOMICROGRAPHS OF WEAR SCARS FROM UNLUBRICATED RUNS

TABLE 11
BALL-ON-CYLINDER TESTS
(240 rpm, 32 min, 77F)

	<u>Argon</u>		<u>Air</u>	
	<u>Dry</u>	<u>Wet</u>	<u>Dry</u>	<u>Wet</u>
	<u>Wear Scar Diameter, mm</u>			
Isooctane	0.27	0.32	0.75	0.95
+ 0.10% AIA*	0.26	0.45	0.45	1.00
Bayol 35	0.34	0.31	0.65	0.77
+ 0.10% AIA*	0.21	0.31	0.32	0.82
	<u>Coefficient of Friction</u>			
Isooctane	0.13	0.22	0.23	0.24
+ 0.10% AIA	v. High	0.19**	0.17**	0.25**
Bayol 35	0.10	0.14	0.16	0.13
+ 0.10% AIA	0.10	0.12**	0.13**	0.14

* 99.6% Methyl Cellosolve
0.4% Glycerine

** More erratic.

in wear rate) but gives a 5% increase in wear scar in wet air (25% increase in wear rate). Note that the effect of either oxygen or water is generally much greater than the effect of AIA. The friction data, also presented in Table 11, shows that AIA generally reduces friction but not very effectively. For example, where the coefficient of friction for Bayol 35 alone was 0.16, for Bayol 35 + AIA it cycled irregularly between 0.10 and 0.16. In wet air, AIA actually gives more friction.

Table 12 gives data on AIA in isooctane containing lubricity additives. These tests were run in room air with uncontrolled humidity. The effect of AIA was quite minor, the wear increasing slightly, the friction decreasing slightly. The lubricity additives have reduced the wear to a much lower level than in Table 11 so that AIA does not have much effect.

Table 13 gives wear data on the effect of Cellosolve alone and also with the trace of glycerine included in AIA. Both isooctane and Bayol 35 were the base fuels. As can be seen in the table, with one exception there was no effect for adding the trace of glycerine, and the exception appears to be due to irreproducibility. In all cases, however, both Cellosolve and AIA reduced wear, although there was little effect on friction. These data correlate best with the dry air data of Table 11.

The final set of data were obtained on the fuel PF-1A furnished by Wright-Patterson Air Force Base. This fuel contained AIA and was extracted as follows: Equal volumes of fuel and distilled water were shaken for two minutes in a separatory funnel, allowed to stand several minutes and the water layer drawn off. This was repeated a second time. The extracted fuel was compared to the unextracted fuel at two loads and under four atmospheric conditions: (a) in room air, (b) in wet air, (c) blown dry with dry air and run in dry air, (d) blown dry and run in room air after equilibrating for three days.

The results were consistent in all cases as shown in Table 14. The unextracted fuel gives less wear, the effect being more pronounced in wet air than in dry. The friction traces show almost no differences in any of the eight comparisons. These data agree with the data in Table 13, AIA reducing wear. They do not agree with the data in wet air which showed AIA to increase wear, both with and without lubricity additives. One can only speculate as to the reason for the differences. Perhaps other additives in the fuel are having an overriding effect; perhaps the extraction removes more than just the AIA. The overall conclusion remains the same. AIA is a lubricity agent but a poor one.

Summarizing all these data, AIA has much less effect on lubricity than do heavy aromatics, corrosion inhibitors, lubricity additives or atmospheric oxygen and humidity. The results shown in Table 11 are believed to be the most definitive. These data were obtained last chronologically and separate the effect of additive and atmosphere most clearly.

TABLE 12

BALL-ON-CYLINDER TESTS

(240 rpm, 32 min, 77F, in Air)

<u>Additive in Isooctane</u>	<u>60 g</u>		<u>240 g</u>	
	<u>WSD, mm</u>	<u>CoFr</u>	<u>WSD, mm</u>	<u>CoFr</u>
None	0.62	Erratic	0.72	Erratic
15 ppm ER-5	0.26	0.17	0.32	0.18
15 ppm ER-5 + 0.1% AIA	0.28	0.14	0.35	0.16
15 ppm ER-3			0.31	0.19
15 ppm ER-3 + 0.1% AIA			0.32	0.18

TABLE 13

BALL-ON-CYLINDER TESTS

(240 rpm, 32 min, 77F)

	<u>Wear Scar Diameter, mm</u>		
	<u>60 g</u>	<u>240 g</u>	<u>1000 g</u>
Isooctane	0.57	0.80	--
+ 0.10% Methyl Cellosolve	0.55	0.54	--
+ 0.10% AIA	0.54	0.55	--
Bayol 35	--	0.41	0.64
+ 0.10% Methyl Cellosolve	--	0.36	0.52
+ 0.10% AIA	--	0.42	0.53

TABLE 14

BALL-ON-CYLINDER TESTS

(240 rpm, 32 min, 77F)

	<u>Dry Air</u>		<u>Room Air</u>		<u>Wet Air</u>	
	<u>240 g</u>	<u>1000 g</u>	<u>240 g</u>	<u>1000 g</u>	<u>240 g</u>	<u>1000 g</u>
Extracted PF-1A	--	--	0.32	0.37	0.32	0.43
PF-1A (With AIA)	--	--	0.26	0.33	0.29	0.38
Extracted PF-1A (Blown With Dry Air)	0.30	0.35	0.31	0.37	--	--
PF-1A (With AIA) (Blown With Dry Air)	0.29	0.34	0.29	0.37	--	--

IV. FUTURE WORK

The work on pure hydrocarbons has shown there are major differences in their lubricity characteristics. Therefore more types of hydrocarbons will be investigated both in the pure state and in blends with paraffinic hydrocarbons. Runs will be made over a wider load range to study their scuffing tendencies.

The effect of diffusivity in the mechanism of corrosive wear is being studied using a mathematical model. This work is expected to result in a publication.

Metallurgy is the next major factor to be evaluated. This work is awaiting arrival of a new four-ball machine.

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